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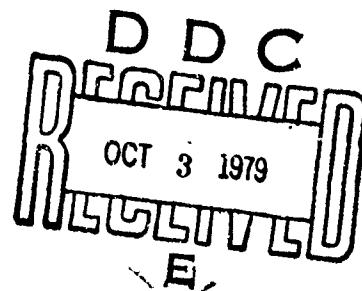
MOISTURE SORPTION AND DIFFUSION IN KEVLAR 49 ARAMID FIBER

BY   JOSEPH M. AUGL

RESEARCH AND TECHNOLOGY DEPARTMENT

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Kevlar is being used increasingly as a reinforcement for fibrous composites. Since moisture affects the mechanical properties of organic matrix composite it is of importance to understand the sorption and transport of moisture in this material. The purpose of this work was to measure the sorption equilibrium of Kevlar with moisture and its diffusion coefficient as a function of concentration. Kevlar 49 has an unusually low diffusion coefficient compared to other polymers, so

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that the moisture transport in composites is governed by the organic
matrix, or by other mechanisms such as microporosity, yet the
equilibrium concentrations as a function of relative humidity are
similar to most epoxy resins.

SUMMARY

This work is part of an effort to characterize mechanical properties and moisture transport in Kevlar fiber reinforced pressure vessels.

The specific purpose of this report is to describe the moisture sorption behavior of the Kevlar 49 aramid fiber. The moisture sorption isotherms and the diffusion coefficient was determined as a function of the moisture concentration. These data are necessary for predicting moisture equilibrium concentrations in the composites for a given environment, and for estimating its internal distribution as a function of time. They are also necessary for estimating the lower limit of moisture permeation through the composite. (The upper limit of the moisture permeation is governed by microporosity, which is also being investigated but not covered in this report.)

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INTRODUCTION

Because of the unusually high strength and stiffness to weight ratios Kevlar 49 and Kevlar 29 aramid fibers have received great interest for military and commercial structural and other applications, such as reinforcement for pressure vessels, tires, armament plates, load carrying members, aircraft panels, and general composite structures.

Moisture is known to affect organic matrix composite especially at elevated temperatures. The reason for this is that moisture usually plasticizes the matrix or it may in some cases also affect the interface between resin and fiber and reduce the interfacial bondstrength.

We have, using micromechanical concepts, quantitatively predicted[1,2], and experimentally verified[3] the changes in the elastic constants of composites from its constituent material properties. One of the important parameters necessary for prediction of composite property changes with time in some specified climatic or storage environment was the moisture diffusion coefficient of the matrix and its dependence on concentration and temperature. Since Kevlar is itself an organic compound capable of sorbing moisture its moisture sorption equilibrium and its diffusion coefficient have to be taken into account for these calculations.

Thus, knowledge of moisture sorption in Kevlar may be important for several reasons:

    a. It will contribute to moisture transport through the composite.

    b. The difference in hygroscopic expansion coefficient between resin and fiber may have a similar or even greater effect than

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1. Augl, J.M., and Berger, A.E., "The Effect of Moisture on Carbon Fiber Reinforced Composites. III Prediction of Moisture Sorption in a Real Outdoor Environment," NSWC/WOL TR 77-13, 1977.
2. Augl, J.M., and Berger, A.E., "The Effect of Moisture on Carbon Fiber Reinforced Composites. IV Prediction of Changes in the Elastic Behavior," NSWC/WOL TR 77-61, 1977.
3. Augl, J.M., "Predictions and Verification of Moisture Effects on Carbon Fiber-Epoxy Composites," NSWC TR 79-43 (in print).

the thermal expansion coefficient in other reinforced composites, which causes stress concentrations.

c. A difference in sorption equilibrium and diffusion rate at rapid temperature changes may lead to an excess of moisture at the interface and give rise to fiber resin debonding.

d. The weight and the dielectric properties will change with sorbed moisture.

Because of the interest the Navy has in this unique material we thought it important that the moisture sorption and diffusion behavior be determined.

EXPERIMENTAL

The moisture sorption equilibria and diffusion coefficients at different concentrations were determined with an electronic Cahn-microbalance which is schematically shown in Figure 1.

A small roll of fibers (about 120 mg) was dried at 105°C in vacuum then it was rapidly transferred into the weighing chamber whereupon a vacuum was applied and the sample chamber temperature was increased to 80°C and held at this temperature till no further weight change occurred. Then the temperature was lowered to the desired measurement temperature and valve No. 2 was closed. The insulation box temperature was kept about 3°C higher than the sample chamber temperature (which was thermostated with a constant temperature circulation bath). The relative vapor pressure was adjusted to the desired level by means of valve V_4 and was measured with a capacitance manometer. Valve V_3 was held open to the 5 buffer reservoir. The weight change was continuously recorded to $\pm$ 0.002 mg. The temperature in the measurement chamber was held constant to $\pm$ 0.5°C.

The sorption and desorption were continued until no further weight change was observable.
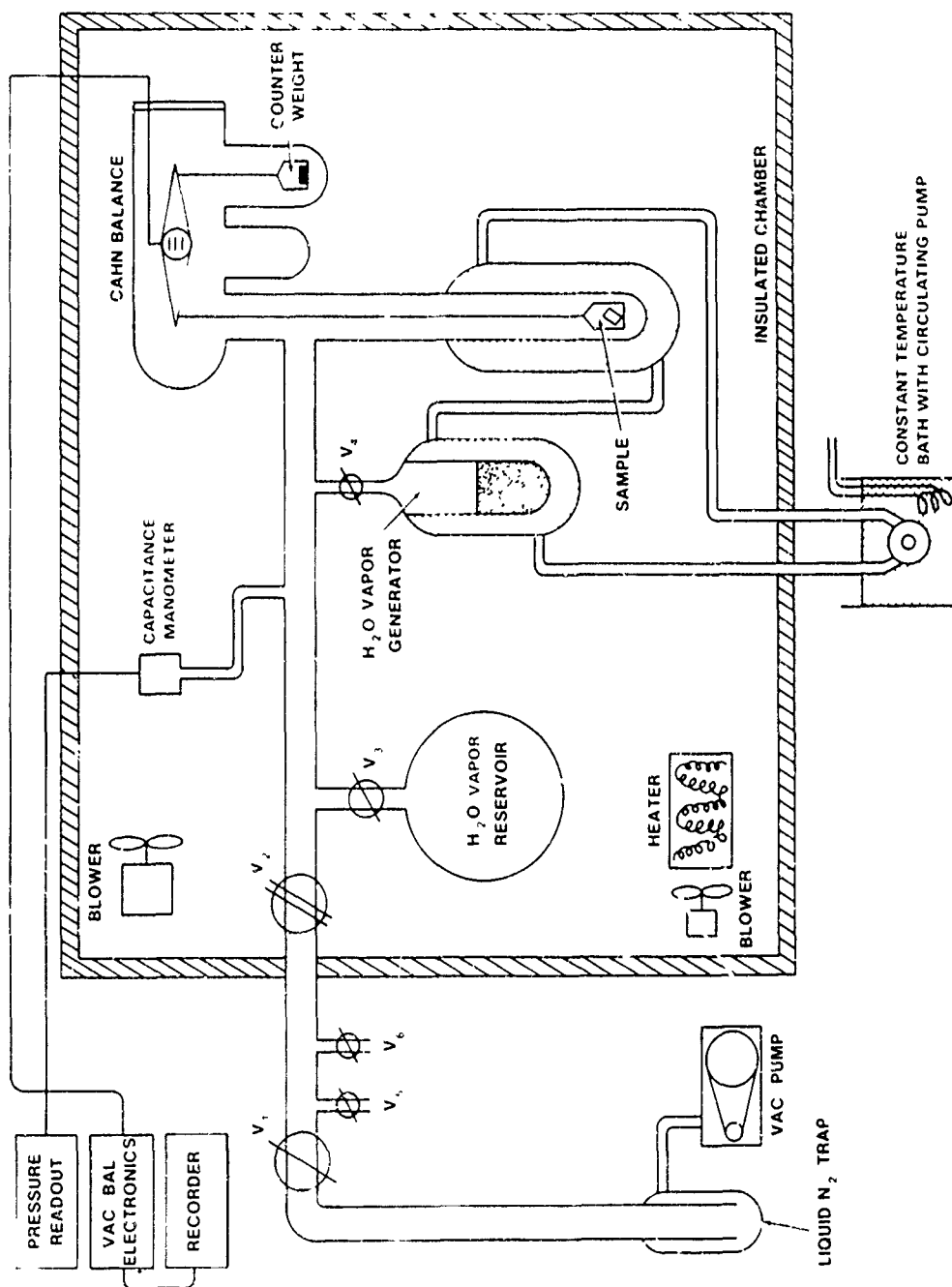
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FIGURE 1 MOISTURE SORPTION BALANCE

DISCUSSION AND RESULTS

Difference in Sorption Behavior

The first sorption experiments on a sample of Kevlar 49 (Lot 16, Ball 172-1 6G45, purchased in 1974) showed an unusual sorption behavior:

1. It absorbed an exceptionally large amount of moisture at high relative humidities (see Figure 2, broken line) and

2. It showed an unusual sorption vs. time $^{1/2}$ curve, although the strand strength was within the specifications of the manufacturer.

It was this alarmingly large moisture uptake and the concern of this effect for composite properties that prompted this investigation. For comparison purposes, we obtained (in 1977) a sample of another lot which was quite different from Lot 16 in its sorption behavior. Subsequently, we requested a sample from Hercules (Bacchus) which behaved identically to the newer DuPont sample, then we received various "old lots" from Lockheed (Palo Alto) that differed somewhat among eachother, but in no way resembled the Lot 16. The absorption curves of these materials at 60% relative humidity and 50°C are shown in Figure 2. We therefore concluded that the material of Lot 16 Ball 172-1 6G45 is probably an unusual exception and the bulk of the measurements reported here were carried out on the sample received from Mr. Jim Culver (Navy representative at Hercules).

Concentration Dependent Moisture Diffusion Coefficient of Kevlar 49

The sorption equilibrium curve of Kevlar 49 as a function of relative humidity is shown in Figure 3 (solid line).

There is a difference in the absorption and desorption times to reach equilibrium. A typical plot is shown on Figure 4, where A stands for absorption and D for desorption. (It is to be understood that the absorption curve starts from 0% moisture concentration and levels out at the equilibrium concentration while the desorption starts out at the respective equilibrium concentration and levels out at zero concentration.)

If there were a concentration independent moisture diffusion both curves would be symmetrical (or the way they are plotted in Figure 4 they
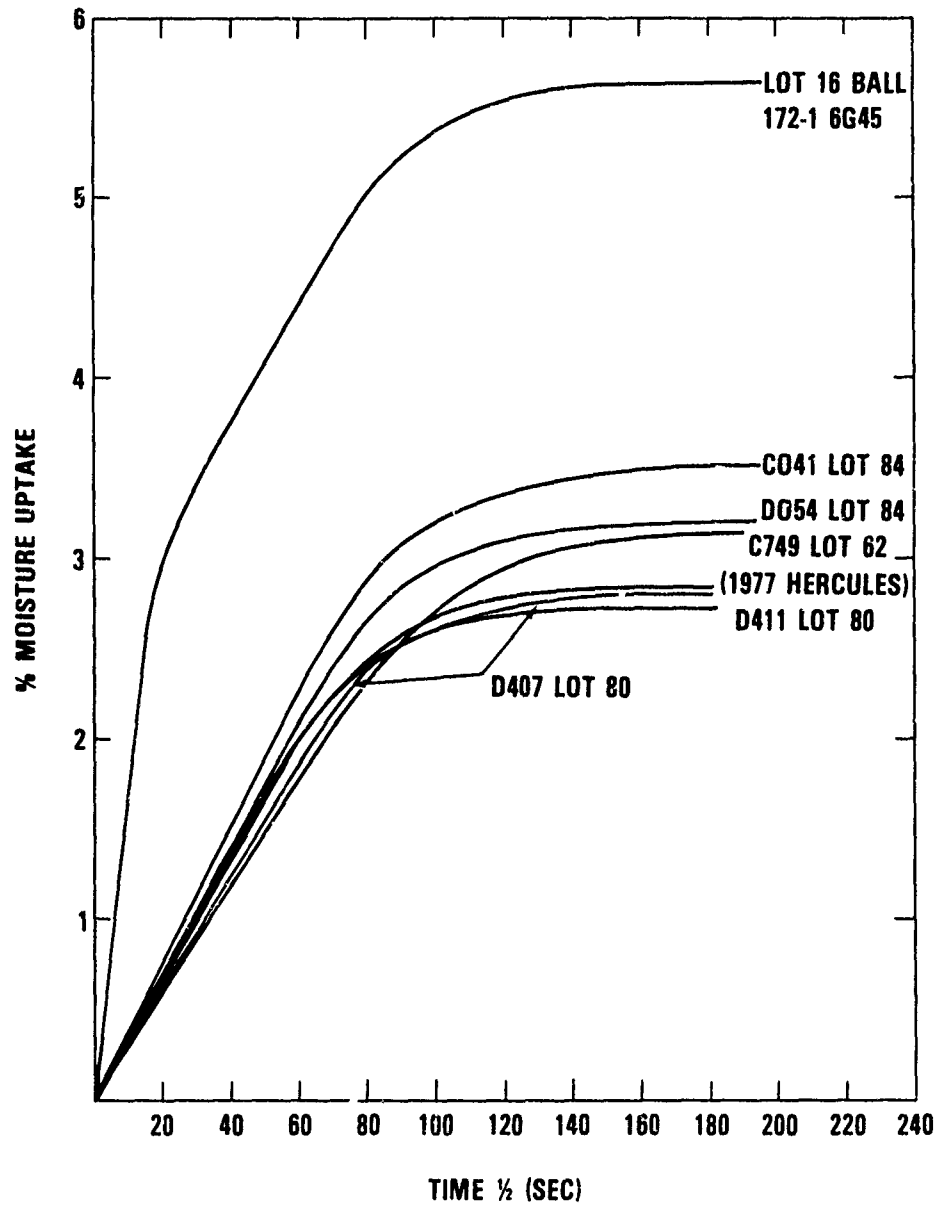
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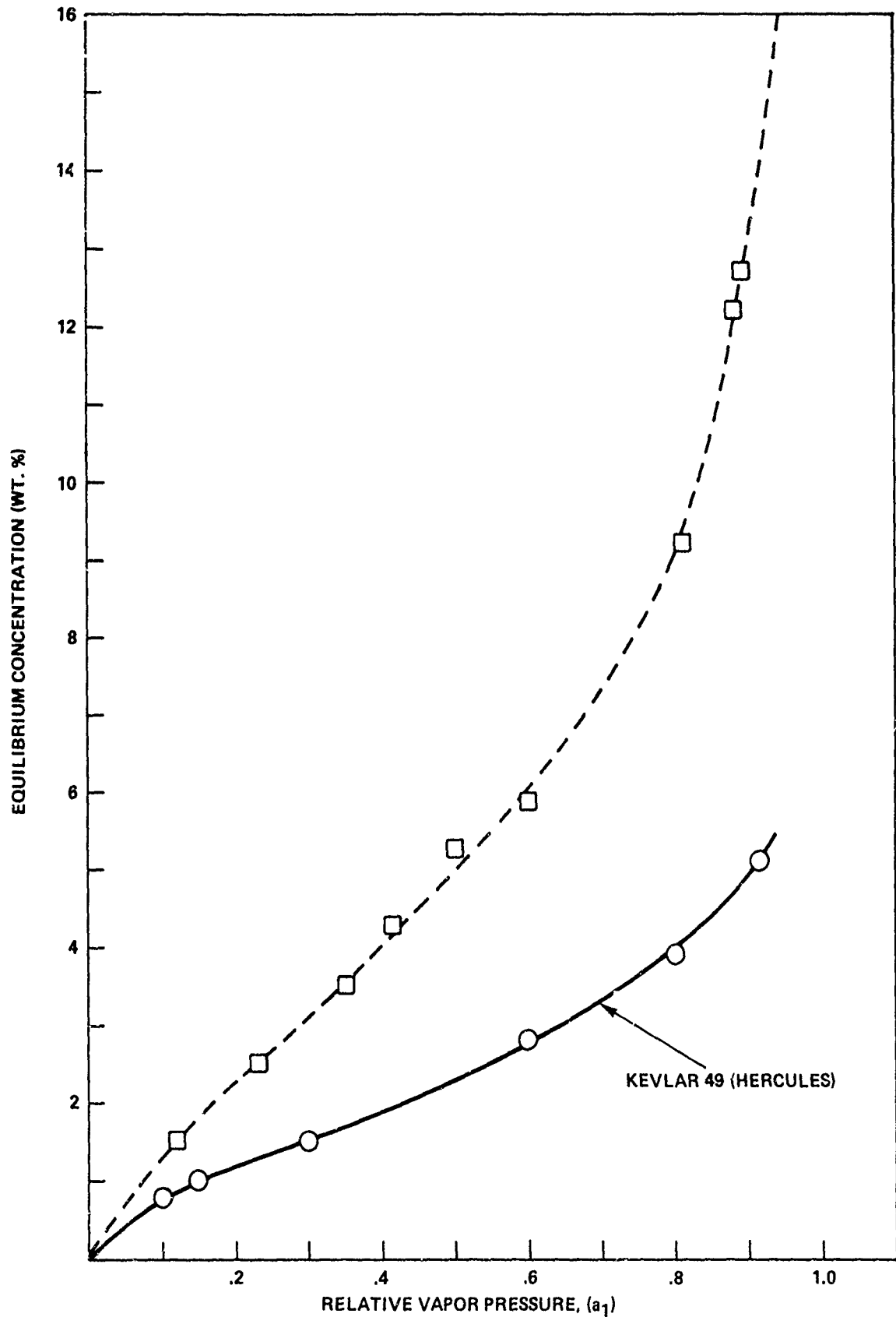FIGURE 2 MOISTURE ABSORPTION IN KEVLAR 49 AT 50° C AND 60% RH

FIGURE 3 MOISTURE EQUILIBRIUM CONCENTRATION OF KEVLAR 49 ARAMIDE FIBER (BROKEN LINE IS AN EXCEPTIONAL, OLD LOT)
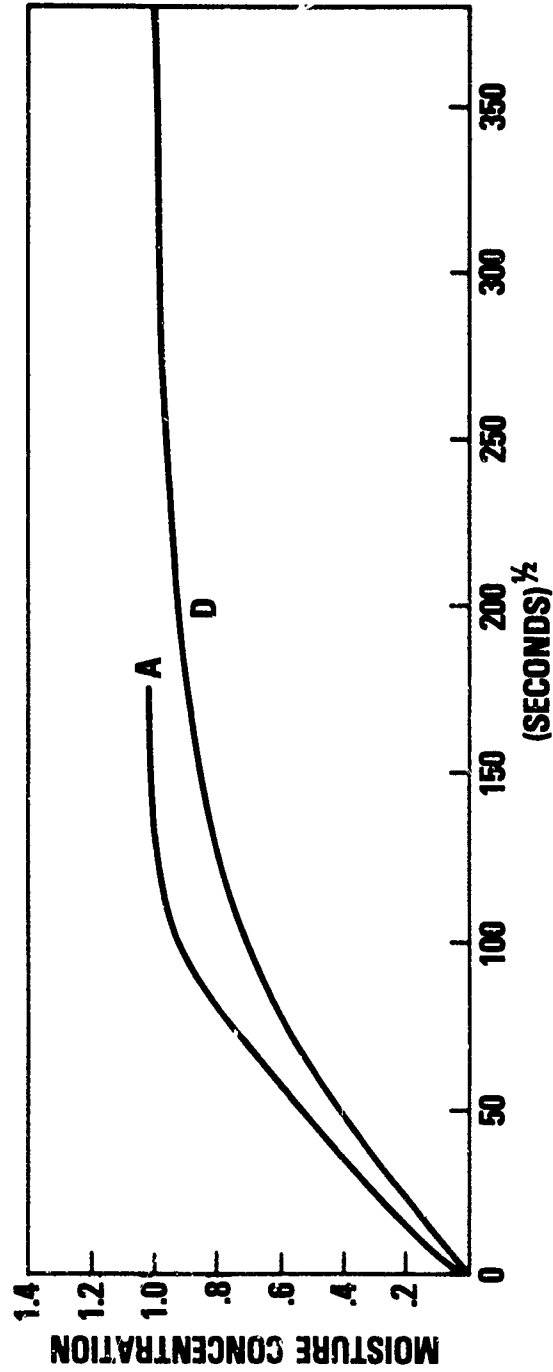
FIGURE 4 ABSORPTION AND DESORPTION IN KEVLAR 49 AT 50° C AND 15% RH

would be identical). Thus, it is obvious that the moisture diffusion coefficient in Kevlar 49 is concentration dependent.[4]

In order to determine the diffusion coefficient of a diffusant in a fiber one has to solve Fick's diffusion equation for a cylinder of infinite length:

$$\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(rD \frac{\partial C}{\partial r} \right)$$

where C = concentration, t = time, r = radial coordinate and D = diffusion coefficient.

The solution for a cylinder exposed to constant diffusant concentration on the surface, where the diffusion coefficient is constant is given in Equation (1):[5]

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{a^2 \alpha_n^2} \exp(-D\alpha_n^2 t) \tag{1}$$

where M_t is the amount of diffusant taken up after time t, M_∞ is the equilibrium concentration reached after infinite time, D is the diffusion coefficient, α_n are the roots of the zero order Bessel function $J_o(a\alpha_n)$, and a is the radius of the cylinder (fiber). Since the radius of the Kevlar 49 fiber is 0.0005969 cm α_1^2 is $(2.4048/.0005969)^2$ = 1.6231 E7, α_2^2 = 8.5524E7, α_3^2 = 2.1018E8, etc.

For small times, one can use Equation (2) for calculating the diffusion coefficient

$$\frac{M_t}{M_\infty} = \frac{4}{\pi^{\frac{1}{2}}} \left(\frac{Dt}{a^2}\right)^{\frac{1}{2}} - \frac{Dt}{a^2} - \frac{1}{3\pi^{\frac{1}{2}}} \left(\frac{Dt}{a^2}\right)^{3/2} + \ldots \tag{2}$$

for long times Equation (3) is more accurate, which uses the first few terms of Equation (1),

$$\frac{M_t}{M_\infty} = 1 - .692 \left(\exp - \frac{5.782\ Dt}{a^2} + .190 \exp \left(\frac{30.5\ Dt}{a^2}\right) \right. $$

$$+ .775 \exp \left(\frac{74\ Dt}{a^2}\right) \ldots \tag{3}$$

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4. Crank, J. "The Mathematics of Diffusion," Clarendon Press, Oxford, 1975, p. 179.

5. Crank, J., ibid, p. 73.

(Equation (3) is also called Hill's equation).

For long time sorption experiments, one can effectively replace the summation of Equation (1) by the first term of the series and one obtains:

$$\ln(1 - \frac{M_t}{M_\infty}) = \ln \frac{4}{a^2 \alpha_1^2} - D\alpha_1^2 t \tag{4}$$

after differentiation of (4) one obtains (5)

$$d[\ln(M - M_t)]/dt = \alpha_1^2 D = -5.783D \tag{5}$$

From Equation (5) one can see that a plot of $\ln(M - M_t)$ vs. time should give a straight line after a sufficiently long time with a slope of -5.783 from which the diffusion coefficient can be determined.

For materials with a very small diffusion coefficient it may be impractical to wait till equilibrium has been reached. In that case, one can use again the first term of Equation (1) for two different "long" times and one obtains Equation (6);

$$(M_2 - M_1) = \frac{4}{a^2 \alpha_1^2} \left[M_2 \exp(-D\alpha_1^2 t_1) - M_2 \exp(-D\alpha_1^2 t_2) \right] \tag{6}$$

where M_1 and M_2 are the amounts absorbed or desorbed after the "long" times t_1 and t_2.

All these equations apply only for a concentration independent diffusion coefficient.

The solution of the diffusion equation where D is concentration dependent is not straightforward and depends on the form of D(C). Various methods for solving practical problems have been described in the literature.[6-11] All these authors determined the concentration dependent D on film samples. Frensdorff[9] has shown (by solving the diffusion equation for a sheet by

6.   Crank, J., and Park, G.S., Trans. Faraday Soc., 45, 240, 1949.
7.   Long, F.A., and Thompson, L.J., J. Polym. Sci., 15, 413, 1955.
8.   Kishimoto, A., and Enda, Y., J. Polym. Sci. A, 1, 1799, 1963.
9.   Frensdorff, H.K., J. Polym. Sci. A, 2, 341, 1964.
10. Duda, J.L., and Vrentas, J.S., AICHE Journal, Mar 1971, p. 464.
11. Barrer, J.A., and Machin, D., Trans. Faraday Soc., 67, 244, 1971.

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a finite difference method) that for the long time experiments, where $\ln(M_\infty - M_t)$ is plotted vs. time, all curves finally become straight lines. He showed the graphs where $D(C)/D(0)$ vary between 1 and 20. Thus the full curves of a sorption and desorption experiment at a constant surface concentration give two important data, namely $D(C)$, the differential diffusion coefficient at the equilibrium concentration, and $D(0)$, the diffusion coefficient when the diffusant approaches zero. Since the concentration gradients for a given M_t/M_∞ in a cylinder and a sheet for a given distance from the center to the outside differ only by a factor of about 2 the analysis of Frensdorff (for sheet geometry) can also be safely applied to cylindrical geometry as long as $D(C)/D(0)$ is not too large. Thus Equation (5) can be used to determine $D(C)$ and $D(0)$ from the corresponding absorption and desorption curves. Equation (6) was tested for its range of usefulness by assuming a concentration independent D and it was found that the error was less than two percent for $M_t/M_\infty < 0.35$; at $M_t/M_\infty = 0.5$ this formula differs by about 7 percent from the theoretical value. Figures 4-9 show typical moisture absorption and desorption curves. Figures 4 and 7 are graphs of percent moisture vs. square root of time, Figures 5 and 8 show graphs of the fractional moisture equilibrium concentration remaining vs. time, and Figures 6 and 9 show graphs of M_t/M_∞ vs. $[D(0)t/a^2]^{1/2}$ where a = the radius of the fiber and the other terms are as defined earlier. The data in the last two graphs are presented in dimensionless coordinates, i.e., all materials which have a concentration independent diffusion coefficient should follow the curve indicated "theoretical." The experimental curves however deviate considerably (using $D(0)$ = 1.54E-12 cm^2/sec), again an indication of a concentration dependent diffusion coefficient.

From these data the following diffusion coefficients were determined: $D(C)$, $D(0)$, and $\bar{D}_i$, where $D(C)$ stands for the differential diffusion coefficient at concentration C, $D(0)$ stands for the diffusion coefficient when the concentration approaches zero and $\bar{D}_i$ stands for the integral or "average" diffusion coefficient determined from the initial portion of the sorption or desorption curves according to Equation (2). The superscripts A and D indicate that the data have been obtained from either the absorption or desorption curves respectively. The subscript S (in Table 1) indicates that the data were obtained from the straight portion of the curves using Equation (5) while those without subscripts were obtained from Equation (6). $D(C)/D(0)$ is also called the relative diffusion coefficient.

Table 1 presents data from the "long-term" solutions of Equations (5) and (6) and Table 2 presents data derived from the "short-term" solution according to Equation 2.

Thus the concentration dependence of the Kevlar 49 diffusion coefficient (at 50°C) is given in Figure 10. Here the concentration is given in terms of the equilibrium vapor pressure (P/P_0). (P/P_0 is also equal to the chemical activity a_1 of the diffusant or if multiplied by 100 it is equal to the relative humidity. To convert this to concentration in terms of g/100g of polymer one uses Figure 3 which relates the equilibrium concentration to the relative vapor pressure.)

FIGURE 5   ABSORPTION AND DESORPTION OF MOISTURE IN KEVLAR 49 AT 50° C AND 15% RH
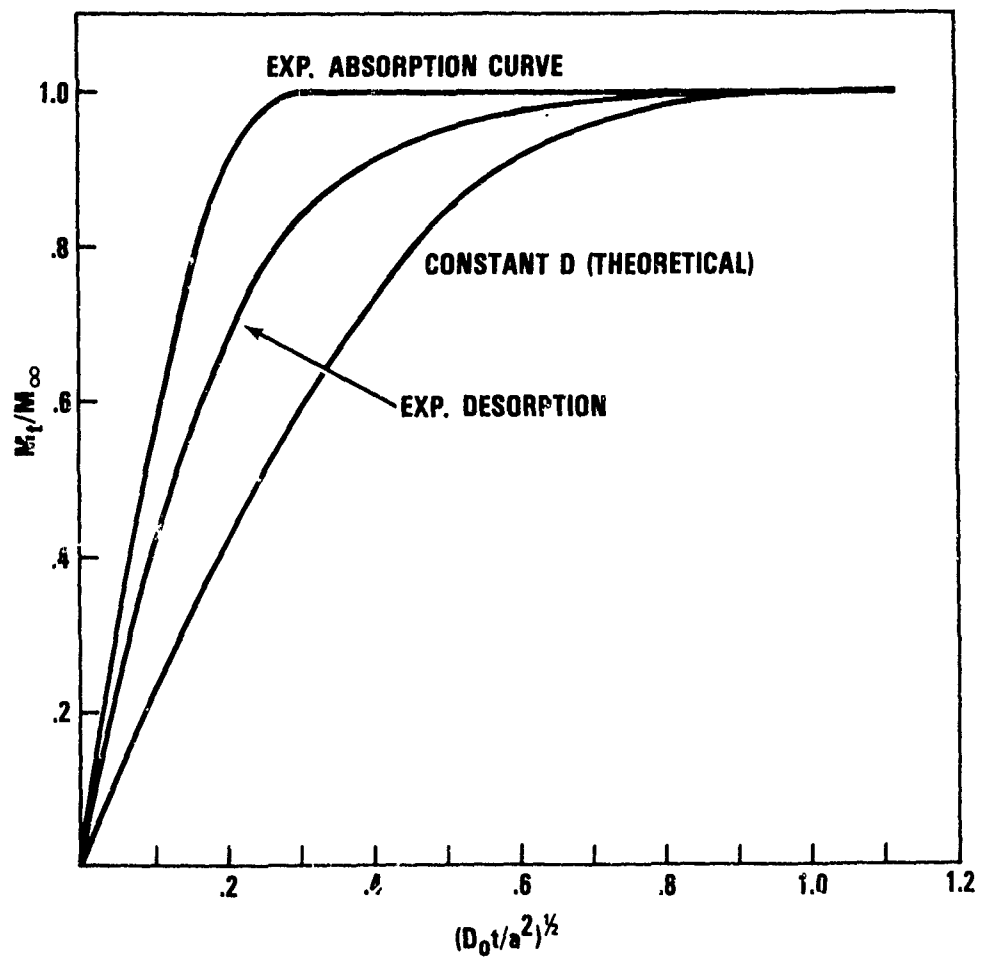
FIGURE 6 THEORETICAL AND EXPERIMENTAL SORPTION AND DESORPTION CURVES FOR KEVLAR 49 (D = 1.54 cm^2/SEC) AT 50° C AND 15% RH

FIGURE 7 ABSORPTION AND DESORPTION OF MOISTURE IN KEVLAR 49 AT 50° C AND 80% RH
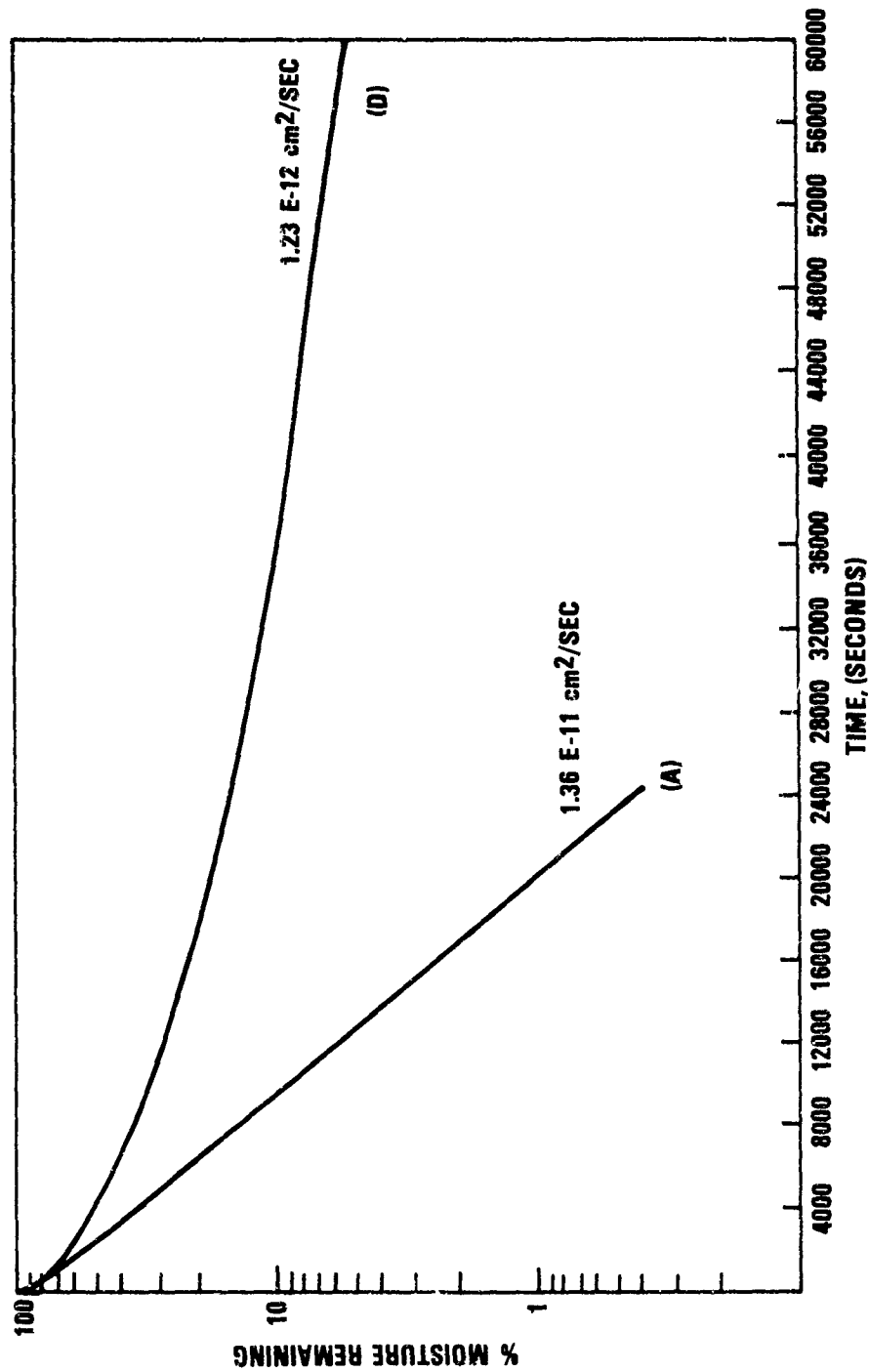
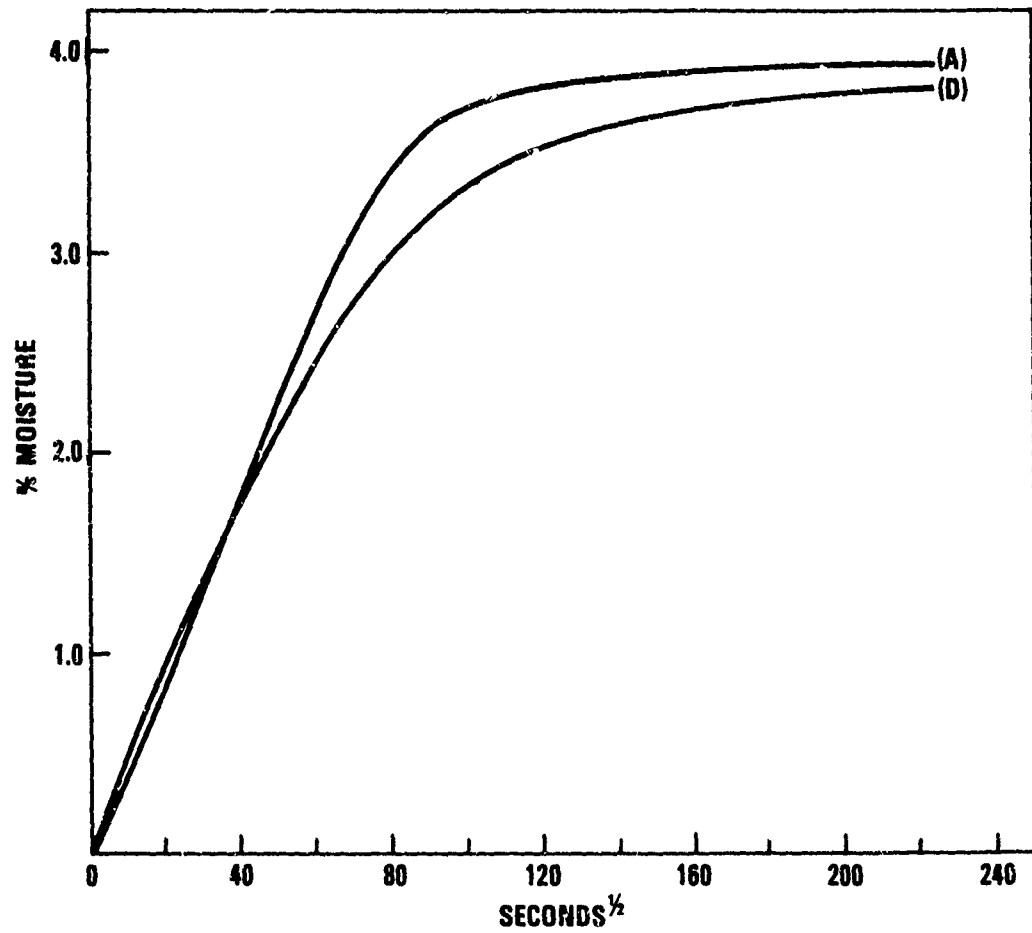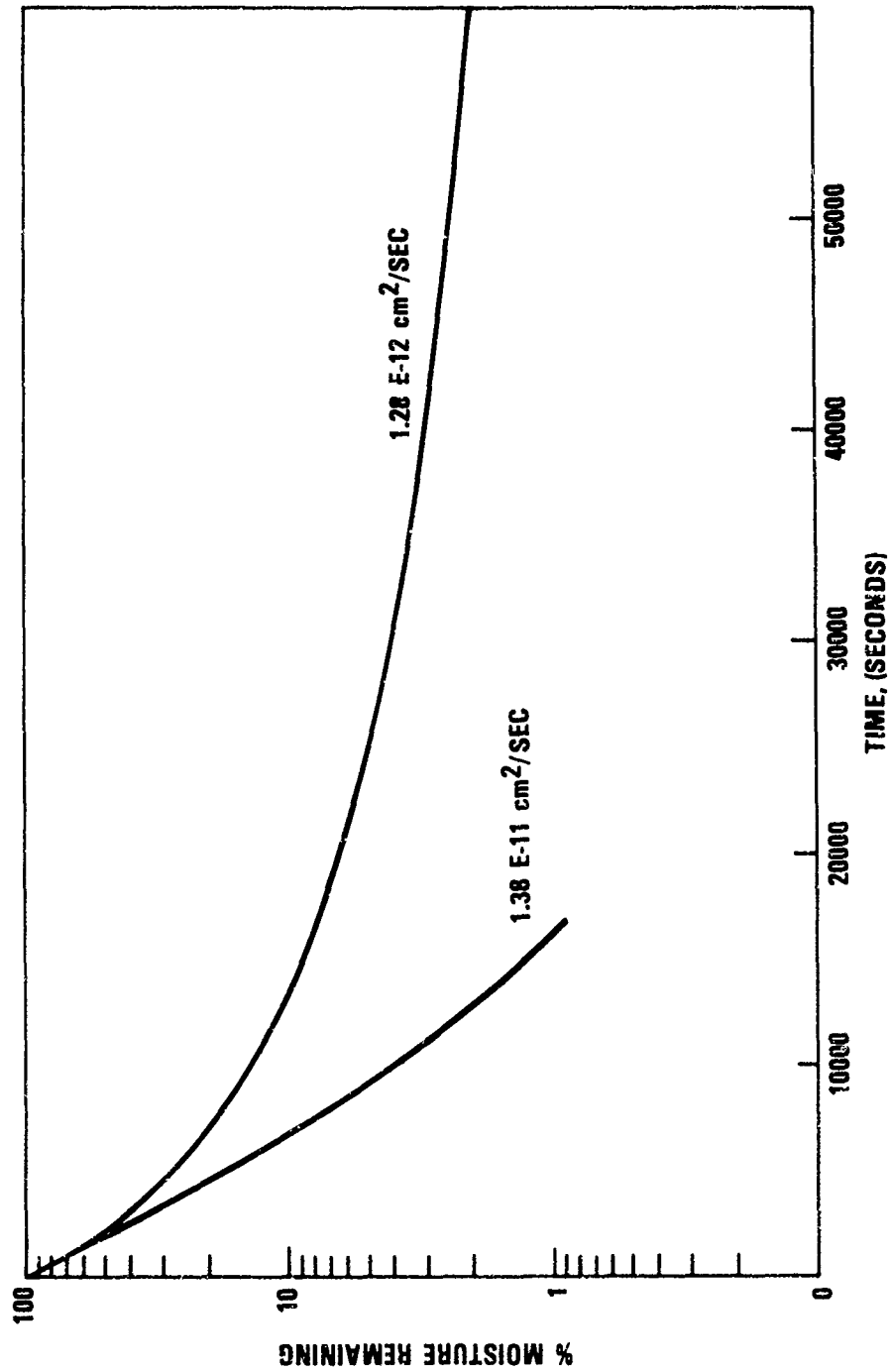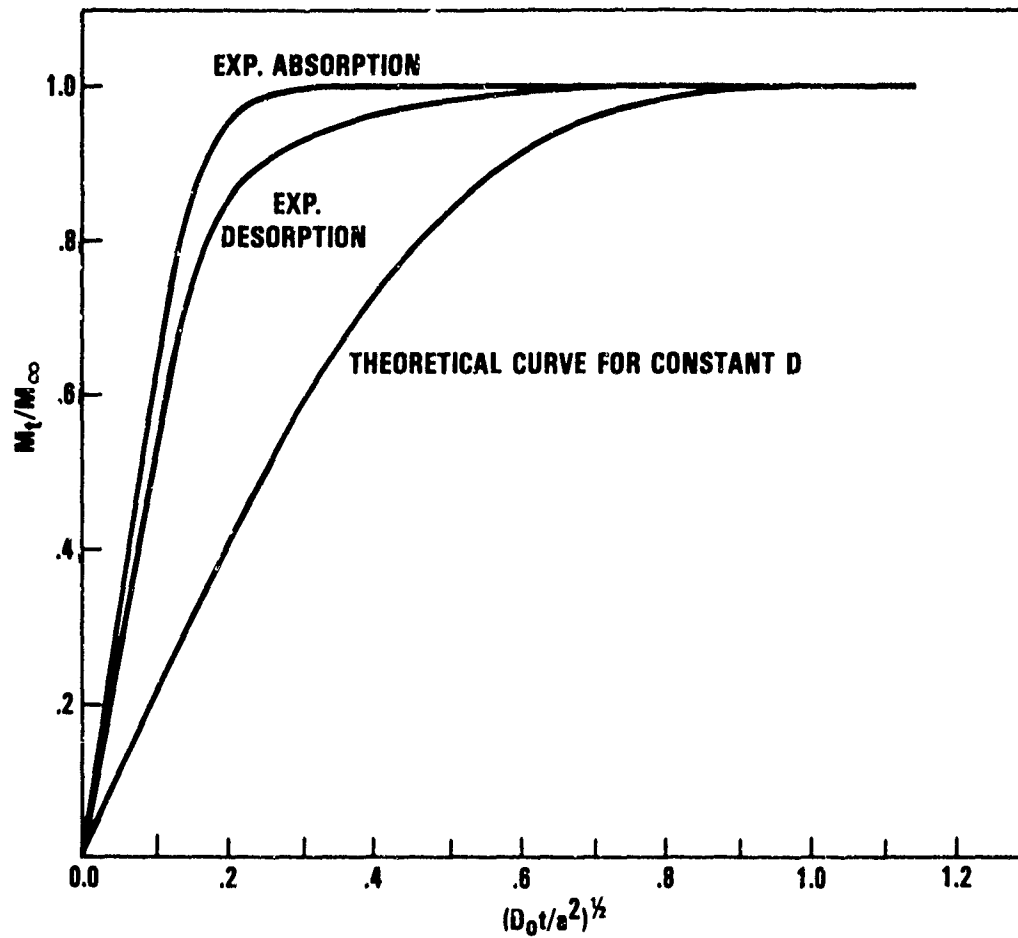FIGURE 8   ABSORPTION AND DESORPTION OF MOISTURE IN KEVLAR 49 (WITHOUT FINISH) AT 50° C AND 80% RH

FIGURE 9 THEORETICAL AND EXPERIMENTAL SORPTION AND DESORPTION CURVES FOR (D_o = 1.54 E-12 cm^2/SEC) KEVLAR 49 AT 50° C AND 80% RH

Table 1. Diffusion Coefficients of Kevlar 49
Determined From Long-Time Sorption And Desorption Experiments

Temp °C	RH %	M_1/M_∞	M_2/M_∞	$D^A(C)$	$D^D(O)$	$D^A_S(C)$	$D^D_S(O)$	$\dfrac{D(C)}{D(O)}$
50	10	.97	.98	1.07E-11	3.00E-12	9.42E-12	1.79E-12	6.12
"	"	.95		1.12E-11	3.08E-12			
"	"	.93		1.09E-11	3.34E-12			
"	"	.91		1.09E-11	3.64E-12			
"	"	.91		1.07E-11	4.72E-12			
"	15	.97	.92	1.26E-11	2.55E-12	1.36E-11	1.23E-12	8.83
"	"	.95	.98	1.26E-11	2.90E-12			
"	"	.93	"	1.23E-11	3.18E-12			
"	"	.91	"	1.23E-11	3.47E-12			
"	"	.91	"	1.22E-11	4.48E-12			
"	30	.98	.92	1.64E-11	4.09E-12	1.68E-11		10.9
"	"	.96	.99	1.59E-11	4.70E-12			
"	"	.94	"	1.57E-11	5.58E-12	–	1.88E-12	–
"	"	.90	"	1.53E-11	5.99E-12			
"	"	.90	"	1.47E-11	6.90E-12			
"	60	.97	.91	1.66E-11	5.01E-12	1.71E-11	1.52E-12	11.1
"	"	.95	.98	1.63E-11	6.80E-12			
"	"	.93	"	1.62E-11	7.67E-12			
"	"	.91	"	1.57E-11	8.50E-12			
"	"	.91	"	1.47E-11	9.89E-12			
"	80	.98	.92	1.47E-11	6.66E-12	1.38E-11	1.28E-12	8.96
"	"	.96	.99	1.67E-11	7.74E-12			
"	"	.94	"	1.72E-11	8.57E-12			
"	"	.90	"	1.68E-11	9.92E-12			
"	"	.90	.91	1.61E-11	1.48E-11			
28	30	–	–	–	–	3.62E-12	–	–
"	60	–	–	–	–	6.42E-12	5.34E-13	–
"	86.2	–	–	–	–	4.95E-12	5.19E-13	–

Table 2. Average Diffusion Coefficients of Kevlar 49
Determined From The Initial Sorption And Desorption Data

| Temp °C	RH %	M_t/M_∞	$\overline{D}_i^A$	$\overline{D}_i^D$	$\overline{D}_i$
50	10	.2	1.27E-11	6.29E-12	9.46E-12
50	10	.3	9.87E-12	4.73E-12	5.17E-12
50	10	.4	8.97E-12	4.84E-12	6.90E-12
50	10	.5	8.86E-12	4.87E-12	6.87E-12
50	15	.2	1.19E-11	5.28E-12	8.59E-12
50	15	.3	1.02E-11	5.54E-12	7.87E-12
50	15	.4	9.95E-12	5.61E-12	7.78E-12
50	15	.5	9.87E-12	5.49E-12	7.68E-12
50	30	.2	1.22E-11	7.25E-12	9.72E-12
50	30	.3	1.20E-11	7.50E-12	9.75E-12
50	30	.4	1.20E-11	7.87E-12	9.94E-12
50	30	.5	1.24E-11	7.74E-12	1.01E-11
50	60	.2	1.24E-11	9.39E-12	1.09E-11
50	60	.3	1.20E-11	9.66E-12	1.08E-11
50	60	.4	1.25E-11	1.01E-11	1.13E-11
50	60	.5	1.30E-11	1.04E-11	1.17E-11
50	80	.2	8.44E-12	1.19E-11	1.02E-11
50	80	.3	9.30E-12	1.06E-11	9.95E-12
50	80	.4	1.04E-11	1.04E-11	1.04E-11
50	80	.5	1.13E-11	1.03E-11	1.08E-11
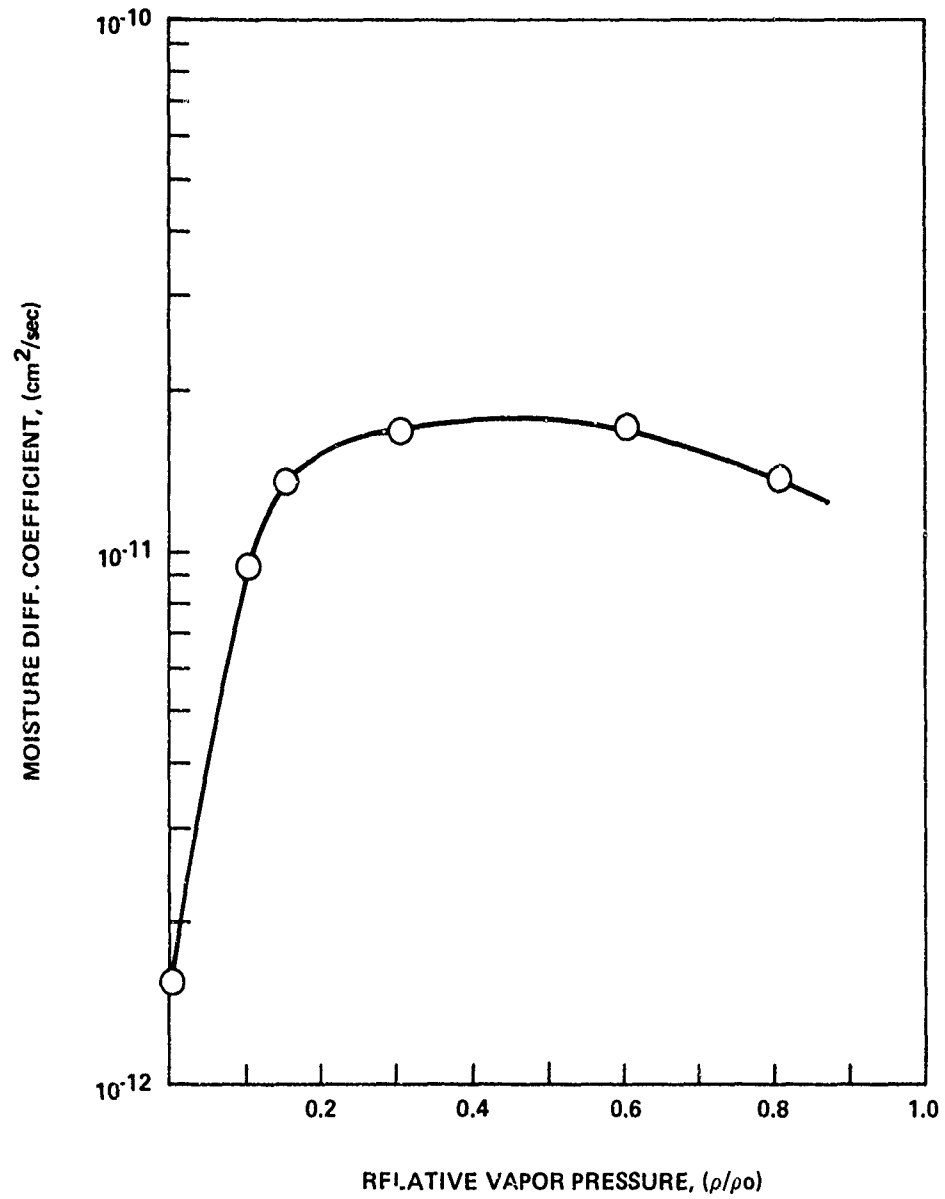
FIGURE 10 MOISTURE DIFFUSION COEFFICIENT OF KEVLAR 49 (AT 50° C)

The diffusion coefficient $D(0)$ of Kevlar 49, when the concentration approaches zero is 1.54 E-12 cm^2/sec with a standard deviation of .292 and a coefficient of variation of 19%. This value was obtained from averaging the data of column 8 of Table 1.

Figure 11 shows the concentration dependence of the relative diffusion coefficient $D(C)/D(0)$.

Since $D(C)/D(0)$ is not more than 12 (see Table 1) the values of $D_S^A(C)$ and $D_S^D(0)$ are considered to be quite reliable and therefore serve as data for comparison for the other data. The data of $D^A(C)$ of column 5 of Table 1 obtained from formula (6) agree quite well with those of $D_S^A(C)$ at least for times when M_t/M_∞ is more than 0.9. On the other hand, the data for $D^D(0)$ from the desorption curves (using the same formula) are too high to be of practical value. It should be noted that the moisture diffusion coefficient for Kevlar is considerably lower than for most other polymers.

It is not surprising that the integral diffusion coefficients obtained from the initial portion of the sorption curves using formula (2) are of qualitative value only and should not be used without further analysis analagous to Kishimoto[8] who expanded the diffusion coefficient in a power series of the form;

$$D(C) = D_0 + k_1 C + k_2 C^2 + k_3 C^3 + \ldots$$

and solving an integral

$$\overline{D}_d (C_o) = 1.85(C_o)^{-1.85} \int_0^{C_o} (C_o - C)^{0.85} D(C) dC$$

to determine the coefficients k_i. His analysis, however, is given only for a plate with infinite extension.

From Figure 11 it becomes apparent that the relative diffusion coefficient $D(C)/D(0)$ goes through a maximum, which could have been guessed also from the intersection of the absorption and desorption curves observed at high relative humidities as shown in Figure 7.

The reason why the diffusion coefficient goes through a maximum with increasing concentration might be explained from the fact that water can form hydrogen bridges and thus can coagulate (i.e., form clusters) inside the polymer matrix. Such a cluster formation is favored with increasing concentration of water, thus reducing the mobility of the diffusant.
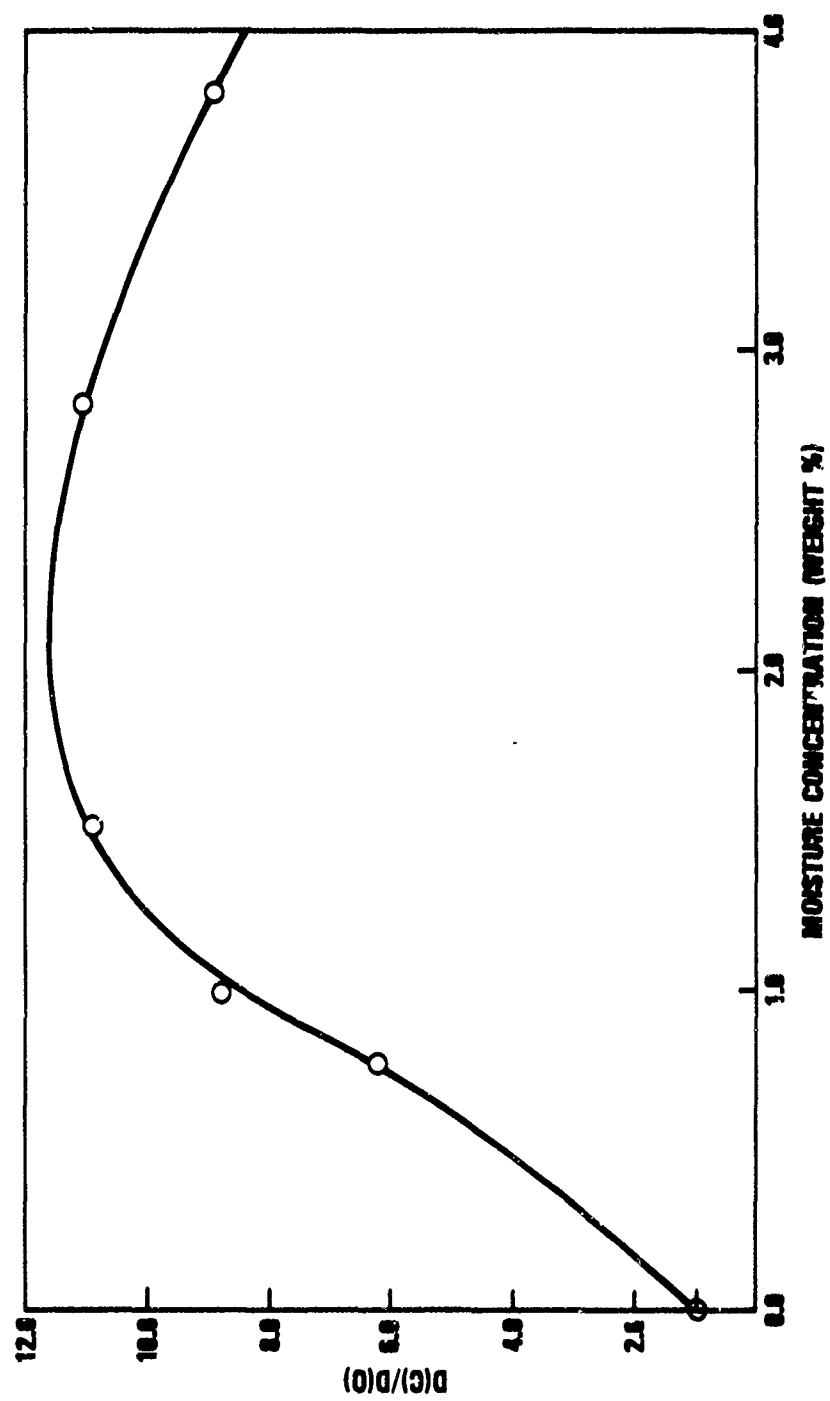
FIGURE 11 CONCENTRATION DEPENDENCE OF THE MOISTURE DIFFUSION COEFFICIENT IN KEVLAR 49 (WITHOUT FINISH) AT 50° C (D(0) = 1.54 E-12 cm^2/SEC)

Based on the statistical thermodynamics of multicomponent systems of McMillan and Mayer[12] and others,[13,14] Zimm and Lundberg[15,16] have derived expressions for determining the degree of clustering in two-component mixtures of polymer and solvent which have the form of Equations (7) and (8):

$$\frac{\Phi_1 \; G_{11}}{V_1} = C_1 G_{11} = \Phi_2 \left(\frac{\partial \ln \Phi_1}{\partial \ln a_1} \right)^{-1}_{p,T} \tag{7}$$

$$\frac{G_{11}}{V_1} = - \Phi_2 \left(\frac{\partial (a_1/\Phi_1)}{\partial a_1} \right)^{-1}_{p,T} \tag{8}$$

where G_{11} is called the cluster integral, a_1 is the chemical activity of the solvent, Φ_1 is its volume fraction, V_1 its partial molar volume and C_1 its concentration.

A tendency for solvent molecules to cluster is revealed by values of G_{11}/V_1 greater than -1. $C_1 G_{11}$ is the mean number of solvent molecules (in this case water) in excess of the mean concentration. Thus the mean size of the cluster is $C_1 G_{11}+1$.

We can use the sorption equilibrium curve of Figure 3 (solid curve) and, from the fiber density ρ = 1.45, derive the curve a_1 vs, Φ_1 which is shown in Figure 12. Figure 13 is a plot of a_1/Φ_1 vs. a_1. By graphical or numerical differentiation one obtains the values of G_{11}/V_1 and $\Phi_1 G_{11}/V_1 = C_1 G_{11}$, which are presented in Table 3 and graphically in Figure 14. Also presented on the same graph are the cluster functions of stretched and unstretched Nylon 66. (The sorption data for Nylon were taken from the literature.)[17]

From these consideratons it is evident that the size of the cluster increases rapidly above an equilibrium concentration corresponding to 60 percent relative humidity. This is about where the diffusion coefficient goes through a maximum.

Effect of Abrasion on the Sorption Behavior

It was suggested that the difference in the sorption curves of Lot 16 and the other Kevlar 49 samples might be due to "kink-bands" that are caused by rough handling of the fibers, specifically when they are forced to bend over

12. McMillan, W.G., Jr., and Mayer, J.E., J. Chem. Phys., 13, 276, 1945.
13. Kirkwood, J.G., and Buff, F.P., J. Chem. Phys., 19, 774, 1951.
14. Flory, P.J., and Kriegbaum, W.J., J. Chem Phys., 18, 1086, 1950.
15. Zimm, B.H., J. Chem. Phys., 21, 934, 1953.
16. Zimm, B.H., and Lundberg, J.L., J. Phys. Chem., 60, 425, 1956.
17. Bull, H.B., J. Amer. Chem. Soc., 66, 1499, 1949.

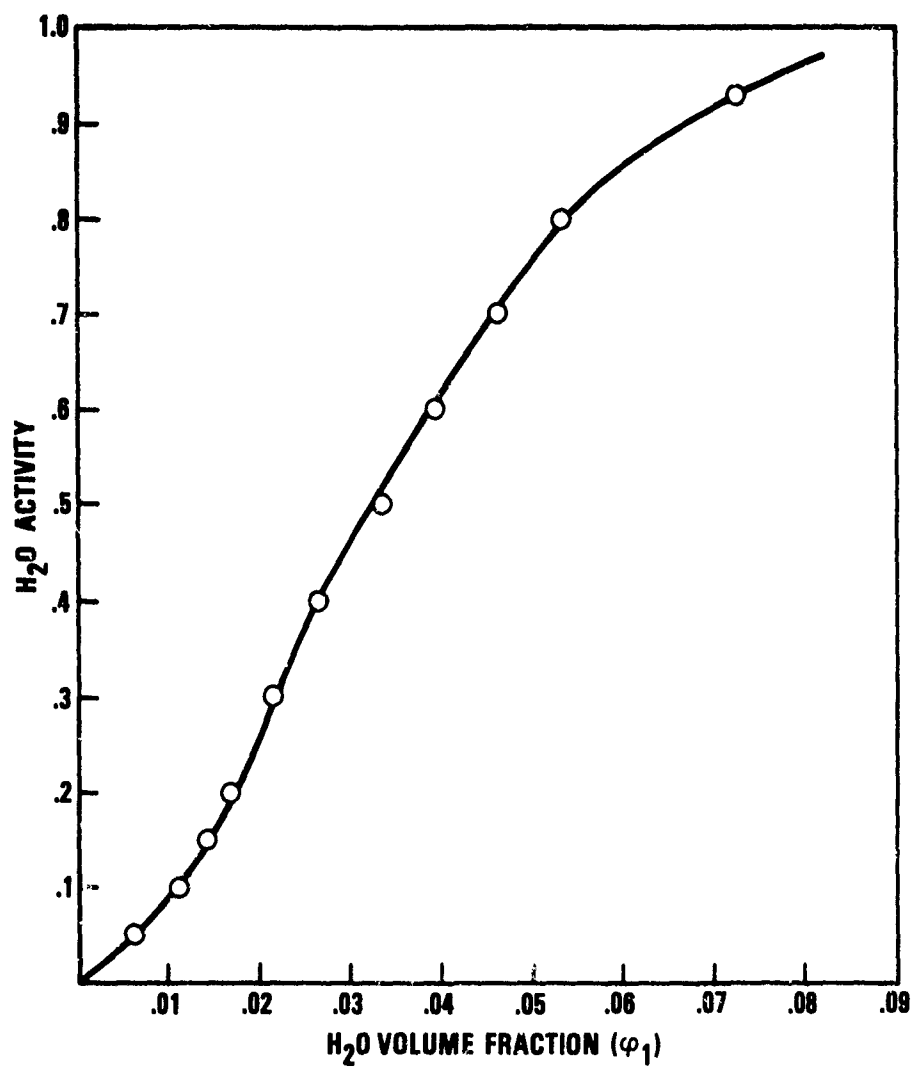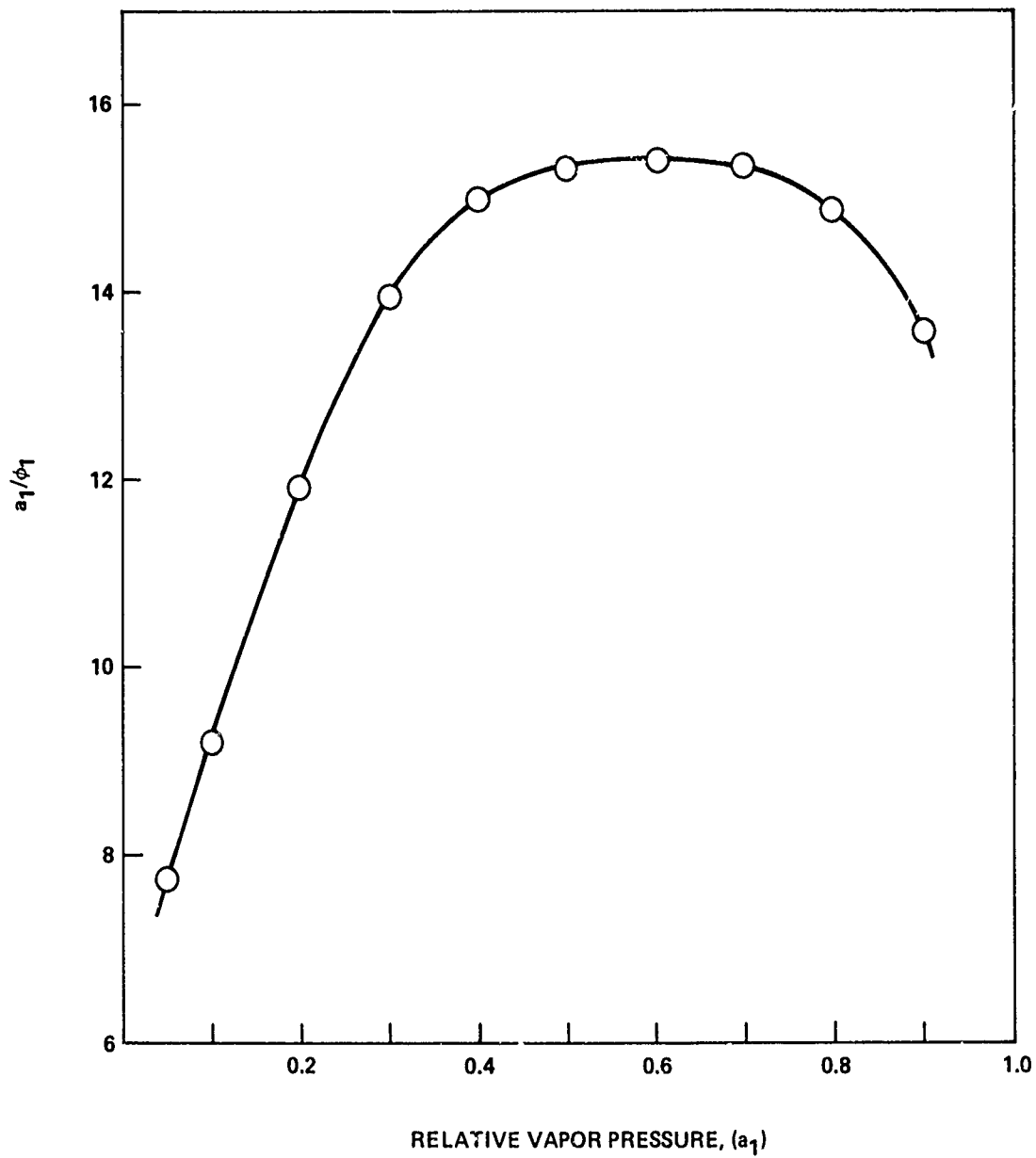FIGURE 12 EQUILIBRIUM SORPTION OF WATER IN ____AR 49

FIGURE 13 ϕ/a_1 VERSUS a_1 OF KEVLAR 49

Table 3. Zimm's Cluster Functions of Kevlar 49
as Functions of Moisture Concentration

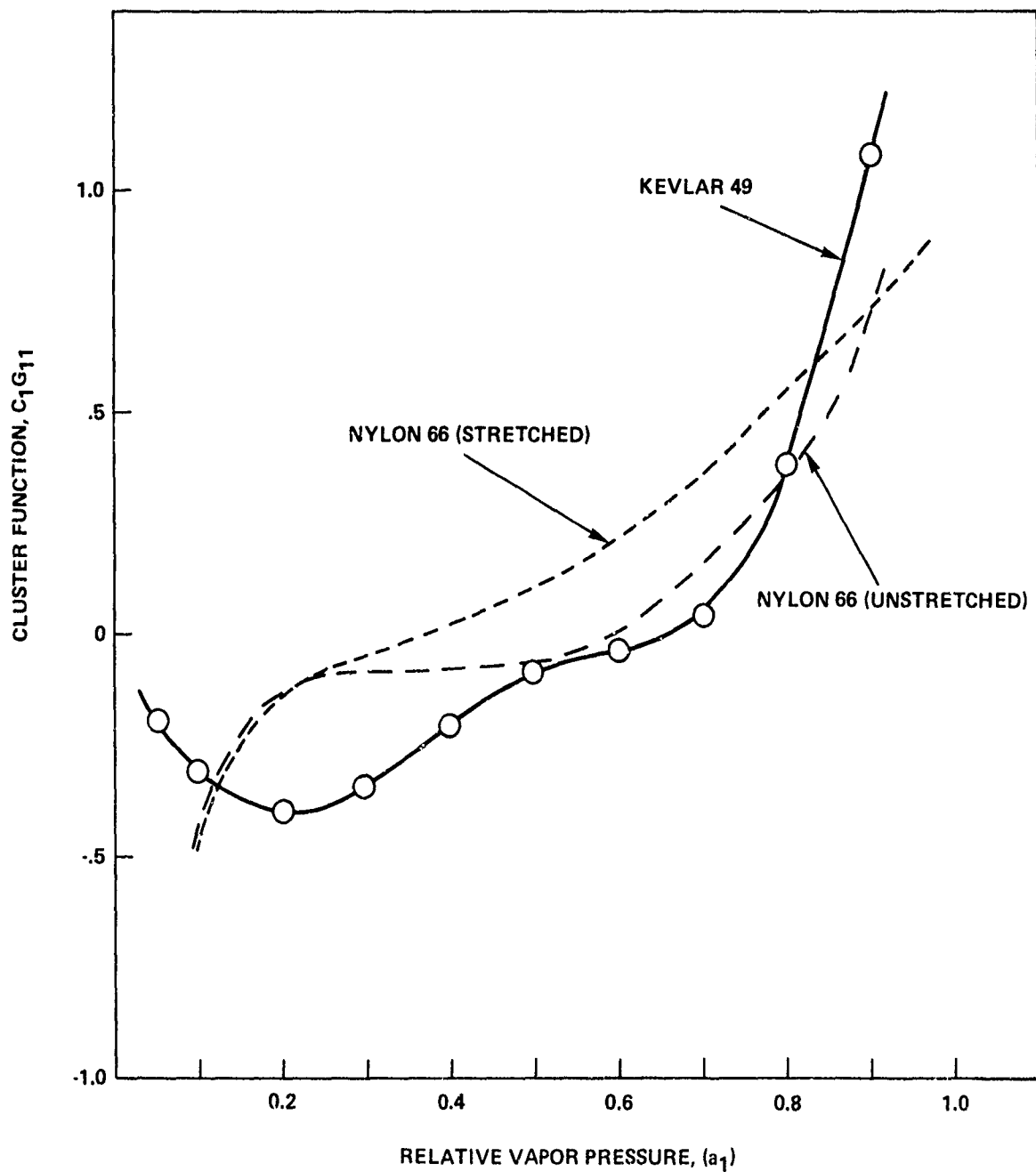| a_1	Weight % H_2O	Φ_1	a_1/Φ_2	Φ_2	$\dfrac{\Delta(a_1/\Phi_1)}{\Delta a_1}$	$\dfrac{G_{11}}{V_1}$	$\dfrac{\Phi_1 G_{11}}{V_1}$
.05	.45	.00648	7.71	.9935	29.37	−30.18	−.196
.1	.76	.0109	9.17	.9891	28.05	−28.74	−.313
.2	1.18	.0168	11.89	.9832	23.54	−24.14	−.406
.3	1.52	.0216	13.91	.9784	15.69	−16.34	−.353
.4	1.89	.0267	14.99	.9733	6.97	− 7.78	−.208
.5	2.33	.0327	15.30	.9673	1.67	− 2.62	−.086
.6	2.80	.0390	15.37	.9610	0.00	− 1.00	−.039
.7	3.30	.0457	15.33	.9543	−2.02	0.928	.042
.8	3.92	.0538	14.87	.9462	−8.60	7.14	.384
.9	4.90	.0663	13.57	.9337	−18.53	16.30	1.081

FIGURE 14 ZIMM'S CLUSTER FUNCTION (C_1G_{11}) OF KEVLAR 49 AS A FUNCTION OF THE
RELATIVE MOISTURE EQUILIBRIUM VAPOR PRESSURE

a small radius. In order to simulate such a condition we have self abraided the fiber by pulling a 1 kg weight (per strand) up and down as indicated in Figure 15, (one cycle is considered one up and down movement). The sorption curves before, after one half and after 7 cycles was measured (see Figure 16). There is undoubtedly a difference in the rate of initial moisture uptake, however, there is no difference in the final sorption equilibrium concentration.

We therefore prefer another explanation that has been suggested: there may be still traces of hygroscopic substances from the spinning process present leading to strong solvation. However, since the spinning process is proprietary this suggestion, though plausible, is only speculation.

Effect of the Finish on the Sorption Behavior

Figure 17 shows the sorption behavior of Kevlar 49 with and without a "standard" DuPont finish. Although it appears that there is a higher degree of moisture sorption on fibers with finish than on fibers without, a comparison with Figure 2 shows however that this difference might fall within the spread of different batches (in Figure 2) that are without finish. Thus, the difference does not appear to be significant.

Test for Fiber Porosity

A yarn bundle of Kevlar 49 was subjected to a mercury intrusion porosity measurement up to pressures of 7000 psi. Figure 18 shows the curve of cm^3 of mercury per gram of fiber vs. absolute pressure, and Figure 19 shows the pore size and distribution curve. The initial mercury uptake is not due to pores in the fiber (since the pore diameters are in the order of the fiber diameters) but due to voids between the packed fibers. No voids are further observed with less than 0.003 microns.
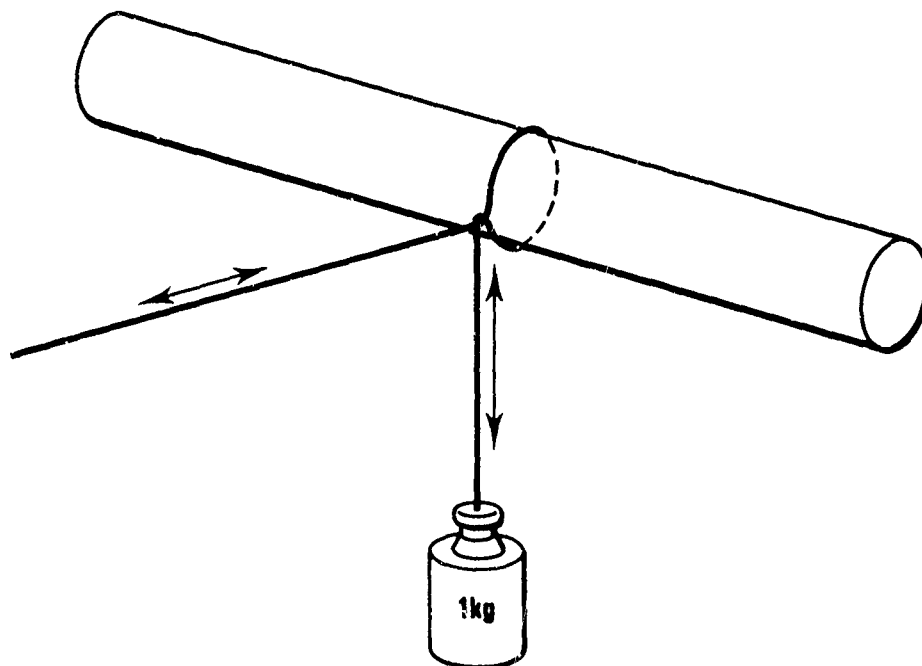
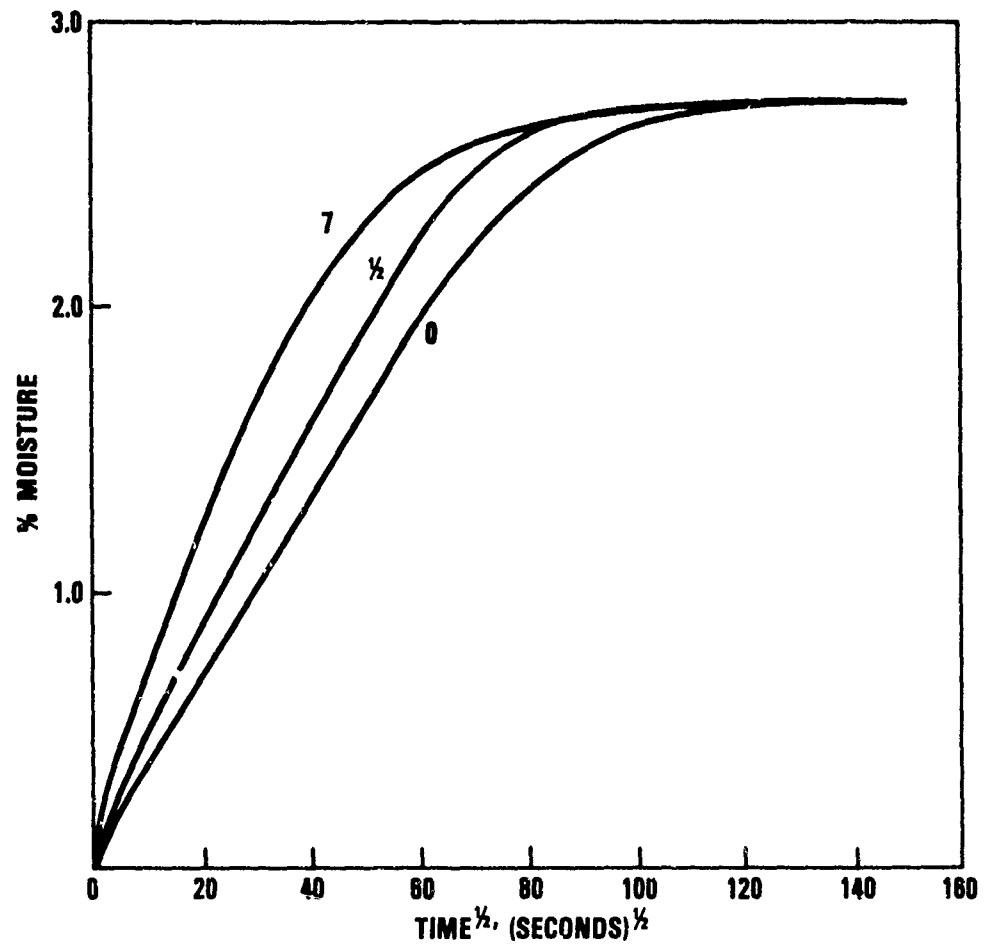FIGURE 15 SELF ABRASION OF A ONE-END KEVLAR 49 STRAND

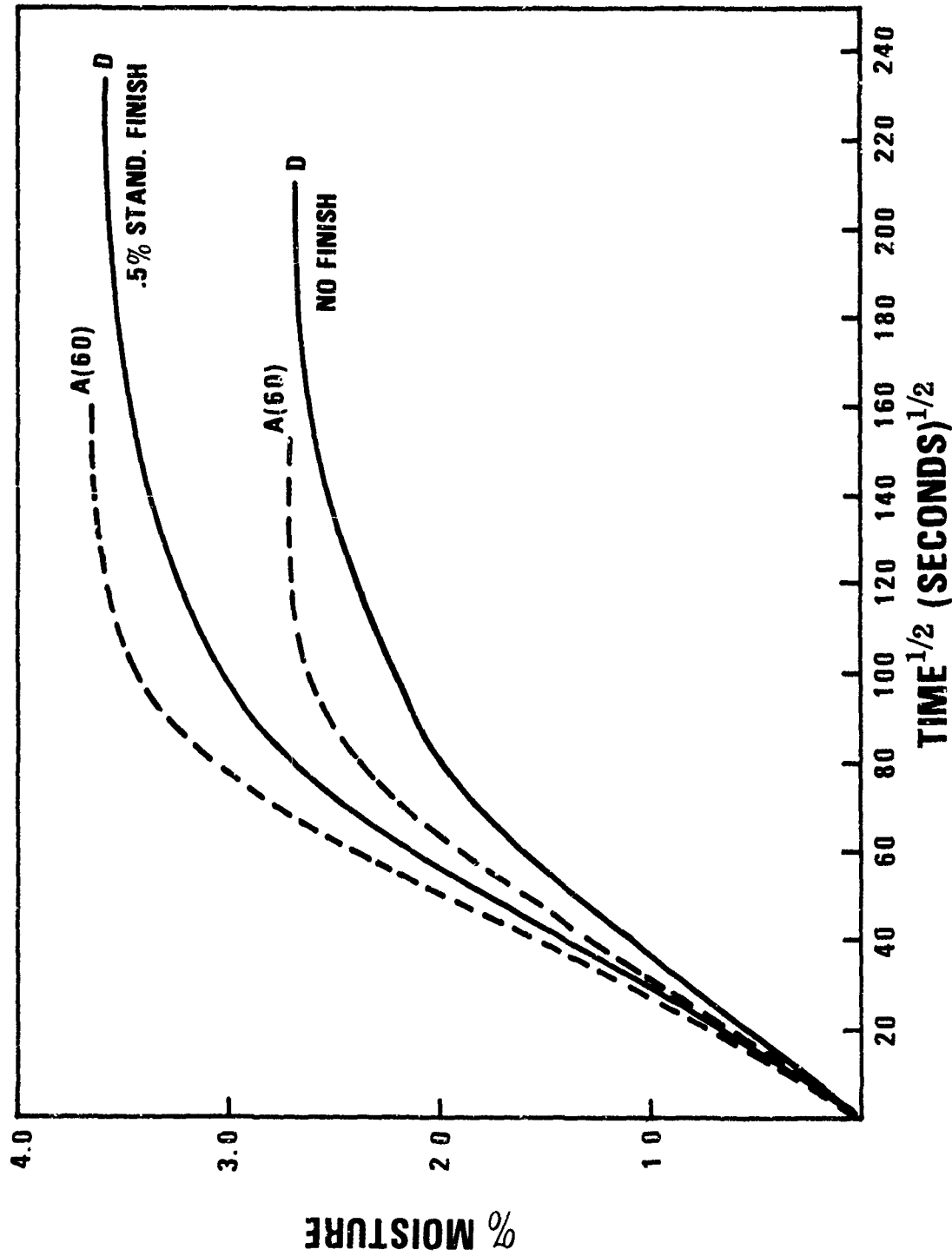FIGURE 16 EFFECT OF SELFABRASION ON KEVLAR 49

FIGURE 17   ABSORPTION AND DESORPTION OF MOISTURE IN KEVLAR 49
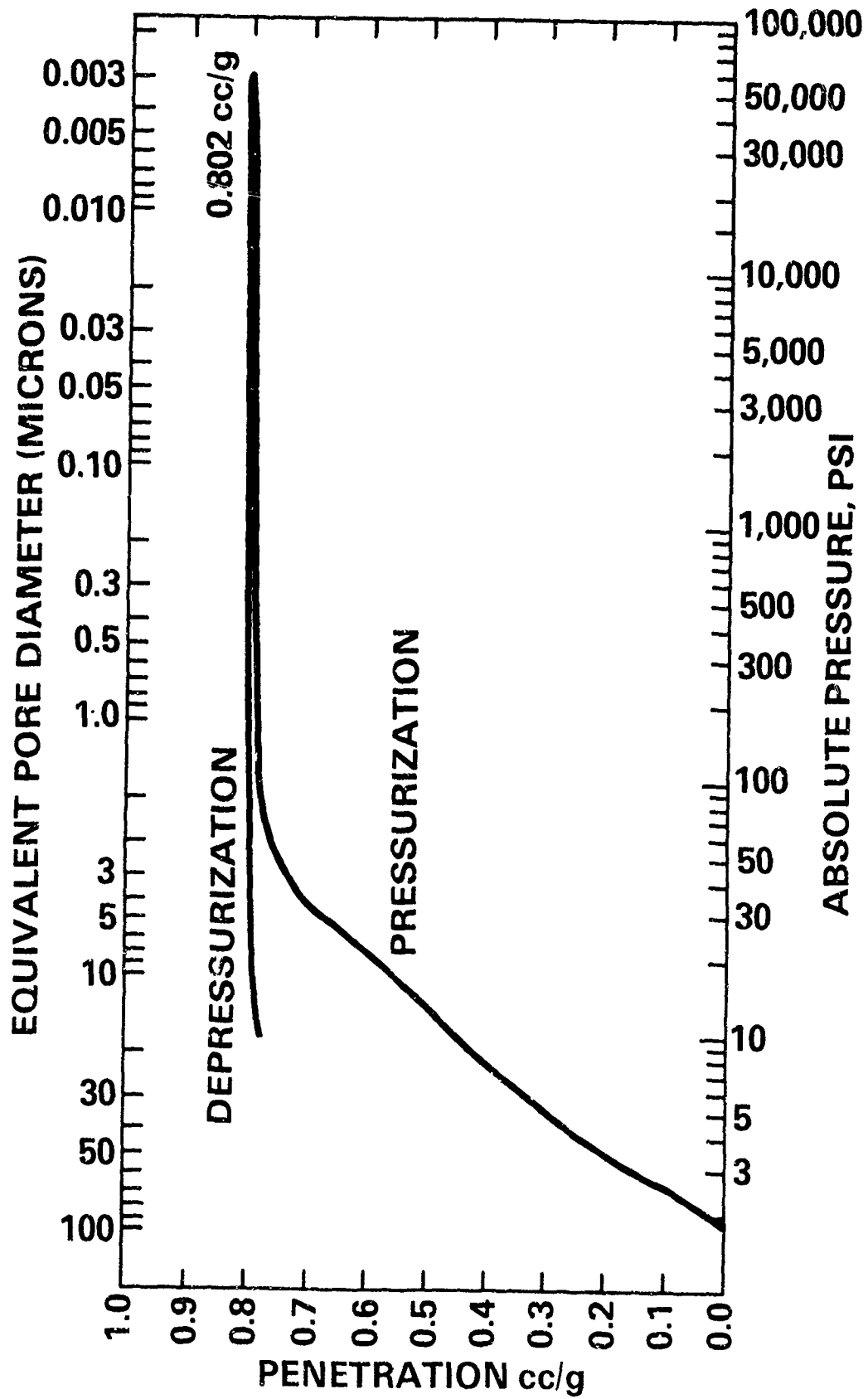AT 50°C FOR FIBERS WITH AND WITHOUT STANDARD DU PONT FINISH

FIGURE 18 MERCURY INTRUSION POROSITY OF KEVLAR FIBER AT 0% RH
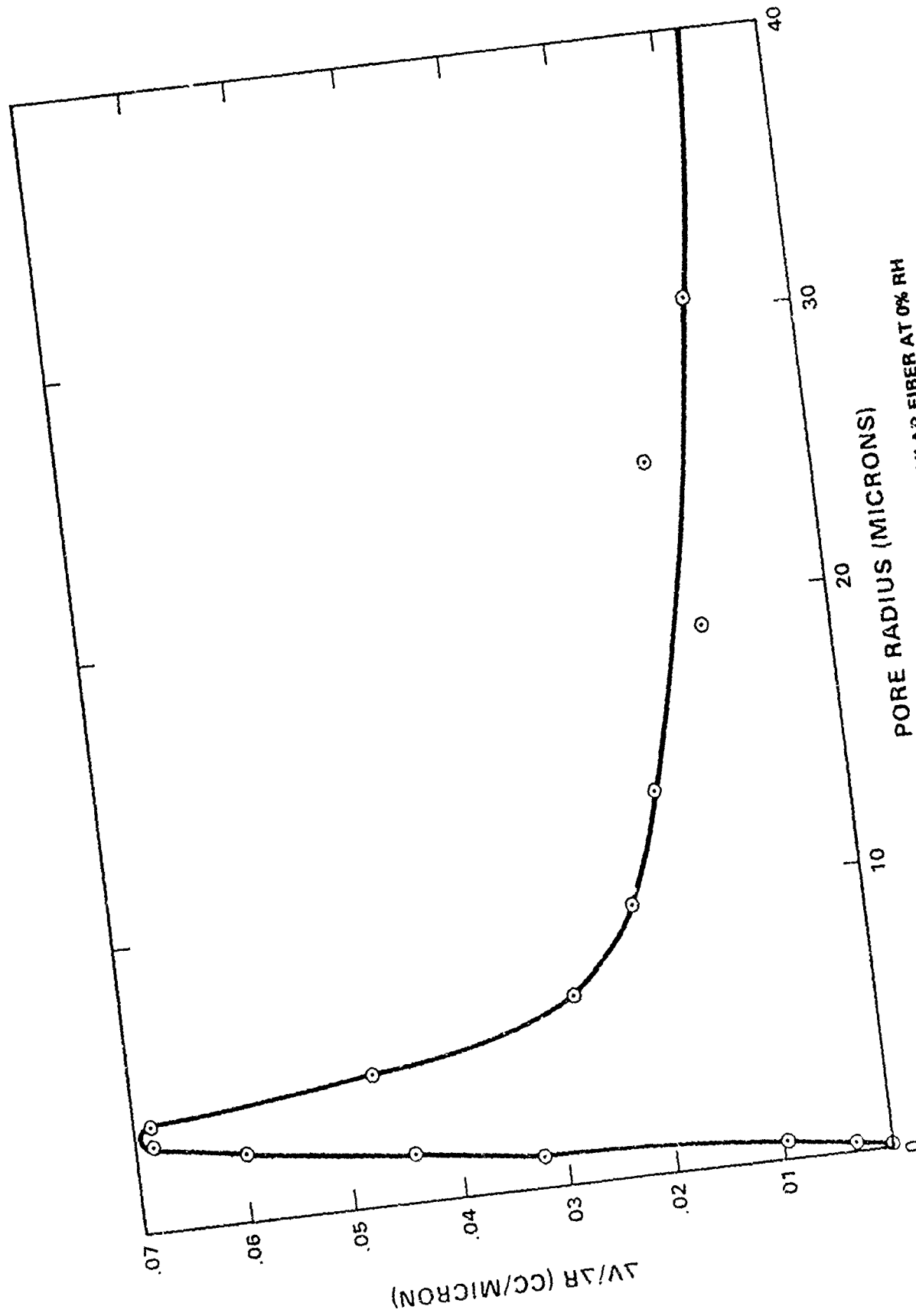
FIGURE 19 PORE-SIZE DISTRIBUTION FOR KEVLAR FIBER AT 0% RH

CONCLUSIONS

1. The moisture sorption equilibrium concentration of Kevlar 49 as a function of relative humidity, and the diffusion coefficient as a function of concentration (at 50° and 28°C) has been measured.

2. The diffusion coefficient is considerably lower than for most other polymers. Thus, in composites, the effective diffusion coefficient is governed by the resin diffusion coefficient and therefore the fibers behave as if they do not contribute to moisture transport, although the total moisture uptake has to be taken into account.

3. One of the measured yarns was quite different from the other samples measured in both the amount of moisture taken up, and in the type of weight gain vs. time$^{1/2}$ curve.

4. Abrasion of the fiber affects the rate of moisture uptake but not the final equilibrium concentration.

5. There is no significant difference in the sorption behavior of yarns with and without sizing.

6. The observed maximum in the diffusion coefficient curve may be explained by the formation of water clusters at high relative humidity.

7. The fiber has no measurable porosity.

ACKNOWLEDGEMENT

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